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APPLICATION OF ESCA TO THE DETERMINATION OF STOICHIOMETRY IN SPUTTERED COATINGS AND INTERFACE REGIONS

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Abstract

X-ray Photoelectron Spectroscopy (XPS) was used to characterize radiofrequency (rf) sputter deposited films of several refractory compounds. Both the bulk film properties such as purity and stoichiometry and the character of the interfacial region between the film and substrate were examined. The materials were CrB_2, MoS_2, Mo_2C, and Mo_2B_5 deposited on 440C steel. It was found that oxygen from the sputtering target was the primary impurity in all cases. Biasing improves the film purity. The effect of biasing on film stoichiometry is different for each compound. Comparison of the interfacial composition with friction data suggests that adhesion of these films is improved if a region of mixed film and iron oxides can be formed.

INTRODUCTION

Sputtering is being used in an increasing number of applications. Both thin and thick films are being deposited as the versatility of the method is recognized. In particular, sputtering has found extensive application in such areas as electronics, corrosion protection, decorative coatings, catalysis, antiwear coatings, and solid film lubrication (1).

In the field of tribology thin films of pure metal, metallic alloys, inorganic compounds, and plastics are sputtered routinely. Refractory carbides and silicides are sputtered onto bearing steels to improve wear life and softer compounds like molybdenum disulfide and PTFE are used as low shear strength lubricant films (2).

Many observers have noted that significant differences in coating properties occurred depending on the deposition conditions. In the field of lubrication, molybdenum disilicide films showed poor adherence and thus poor antiwear properties until a substrate bias was applied during film deposition (3). The friction and wear behavior of rf sputtered films of CrB_2 and MoS_2 were also found to depend on deposition conditions (4). In view of the importance of these observations to tribology and also due to the importance of the chemistry or purity of sputtered films in other areas such as electronics or catalysis, a study of the chemistry of sputtered films was undertaken.

Chemical analyses of sputtered films are infrequently done. Rather, indirect measurements such as resistivity are more often employed. Direct measurements either require prohibitively thick films or removal of the film from the substrate - often difficult and tedious (5). X-ray photoelectron spectroscopy (XPS) or ESCA is ideally suited to the study of sputtered film composition. Because it is surface sensitive, thin films can be studied without elaborate preparation. When used in conjunction with sputter etching, XPS can provide information on variations of composition with depth. Information on chemical bonding as well as composition is available by observing shifts of the electron binding energies (6).

The objective of this investigation was to use XPS to characterize radiofrequency (rf) sputter deposited films of materials that are of current interest in the field of lubrication. Both the bulk film properties such as purity and stoichiometry and the character of the interfacial region between the film and substrate were examined. The materials were chromium boride (CrB_2), molybdenum disulfide (MoS_2), molybdenum carbide (Mo_2C), and molybdenum boride (Mo_2B_5), on both oxidized and sputter cleaned 440C steel substrates. The results are compared to data taken from the literature on the friction and adhesion of the films (3, 4, 7).

APPARATUS AND PROCEDURE

Radiofrequency (rf) Sputtering Apparatus

The sputtering of the materials used in this investigation was conducted in a commercial rf diode apparatus (3) operating at 13.56 MHz. The material to be sputter deposited is in the form of a hot pressed compact which was commercially purchased. The specimen to be coated is placed 2.5 centimeters directly below the target on an electrically insulated block. An additional voltage from 0 to -1500 volt dc may be applied directly to the specimen either for specimen cleaning by dc sputter etching or for biasing the specimen during film deposition and growth. Provision is made for rotation of the entire substrate table so the specimen may be moved out from under the target for cleaning. The target also can be cleaned in this manner without contaminating the specimen. The system is mechanically forepumped and oil diffusion pumped through a liquid nitrogen cooled baffle. During deposition, high purity argon (99.9995 percent) was bled continuously into the system through a leak valve and a dynamic pressure balance between the pumping system and argon leak of approximately 20 microns was maintained in the bell jar.

Prior to actually starting deposition, the target was cleaned by rf sputtering until little pressure rise due to outgassing occurred. Following target cleaning, the rf was turned off and the specimen cleaned if desired by dc sputter etching at -1200 volts for 15 minutes. Following specimen cleaning, the selected power and bias voltage parameters were set and the specimen rotated back under the target and deposition initiated.

STAR Category 27

X-Ray Photoelectron Spectroscopy

General principles. - After deposition, the films were analyzed by X-ray photoelectron spectroscopy (XPS). The principles of XPS are detailed in Refs. 6 and 8. Briefly, X-ray photons striking an atom in the surface cause it to emit an electron. The electron will leave the atom with a kinetic energy K, which is the difference between the incident photon energy $h\nu$ and the binding energy E_B of the electron in the atom. Each energy level in every atom in the analyzed region contributes an electron at its binding energy. These electrons form peaks in the XPS spectrum which are identified by the usual spectroscopic notation in the discussion and figures to follow.

The binding energies are characteristic of the atom excited and depend on the oxidation state of the atom. Thus, if the electron energies K emitted from a sample are measured and $h\nu$ is known, the atoms in the sample may be identified and information about the compounds in which they exist extracted by comparing the measured binding energies with binding energies measured previously on standard samples. Because of the low kinetic energies (<2 keV) of the electrons, the atoms more than 20 Å below the surface of a solid do not contribute to the spectrum.

The intensity of electron emission from any energy level in a particular chemical species is proportional to the photoelectric cross section for that level, the escape depth of the electrons in the sample and the concentration of that species. The cross section is different for every energy level in every atom, but does not vary with the oxidation state of the atom. The escape depth depends on the electron's kinetic energy and the absorbtion properties of the specimen as a whole: the so-called matrix effects. The technique is thus semiquantitative.

Apparatus. - The particular apparatus used here consisted of a commercial electron energy analyzer, described in Ref. 9, and an X-ray source in a vacuum system designed to accommodate a variety of samples. The system is a stainless steel bakeable ultrahigh vacuum system. It is ion pumped and incorporates a titanium sublimation pump. An ion gun in the system was used to gradually sputter away the sample surface and determine the composition as a function of depth. The arrangement of the system is shown schematically in Fig. 1(a).

The X-ray source had a magnesium target with a characteristic energy, $h\nu$, of 1253.6 eV. It was operated at 10 kV and 40 mA and is regulated in such a way that the X-ray flux is held constant despite voltage fluctuations. The electron energy analyzer is a retarding grid followed by a double pass cylindrical mirror analyzer (CMA) whose axis is normal to the X-ray beam. The energy of electrons passed by the CMA is fixed (50 eV here), and the retarding grid voltage is increased linearly with time. This voltage drives the x-axis of an x-y recorder. Electrons passing through the CMA cause pulses in an electron multiplier. These pulses are fed to a ratemeter which drives the y-axis of the x-y recorder. The recorder thus plots a spectrum of electron current versus energy with peaks at each electron binding energy. A block diagram of the apparatus is given in Fig. 1(b).

Data analysis and calibration. - The peak widths depend on the pass energy of the CMA. In this study, peak widths are no less than 1.5 eV full width at half maximum. The peak maxima can be located to ±0.1 eV at best. The energies are referenced to the carbon (1s) line at 284.0 eV and the gold (4f 7/2) line at 84.0 eV. A reasonable estimate of the probable error of the binding energies quoted here is ±0.3 eV. The reproducibility of peak height values was determined by measuring several characteristic peaks from a sputter deposited film at six different locations on the film. The probable error in the peak heights ranged from ±2 to ±10 percent, the larger value being for peaks near the limits of detectability. Peak ratios were generally good to ±10 percent or less.

Because the chemical shifts in binding energy are sometimes comparable to the width of the peak, a peak is frequently broadened without being resolved into two distinct peaks. In most cases these broadened peaks could be resolved using an analog curve resolver. In this way binding energies and peak heights for all components of a peak could be obtained.

The binding energy characteristic of an element in a particular compound must be determined by measurement on that compound. Samples of the pure material or powder scraped from the actual sputtering targets were used here. These binding energies are quoted in the text and figures as appropriate. Reference will also be made to the ratios of peak heights. These peak heights were determined by XPS measurement of a standard except in the case of Mo_2C. The material used to mount the Mo_2C powder interfered with the carbon peak height measurement. Therefore, the ratio of C(1s) to Mo(3d 5/2) peak heights in Mo_2C was calculated from the theoretical photoelectric cross sections (10). The work of Brillson and Ceasar (11) indicates that this calculated value should be within ±10 percent of the true value.

Ion Etching and Depth Profiling

An ion gun in the system was used to gradually sputter away the sample surface and determine the composition as a function of depth. The gun used argon ions of 5 keV energy. The ion gun was equipped with deflection plates which permitted the beam to be scanned in a raster pattern while sputtering. Thus a uniform sputtering rate was obtained over an area larger than the area analyzed by XPS. The sputtering rate was measured on an anodized tantalum oxide film 1000 Å thick and on a 550 Å gold film evaporated onto a silicon substrate. In both cases the sputtering rate was 5 Å/min. The width of the gold-silicon interface was found to be 125 Å which is taken to be the depth resolution characteristic of this study.

Procedure

After a film was sputter deposited the disk was rinsed with ethyl alcohol and mounted in the spectrometer vacuum chamber. The base pressure in the chamber was allowed to

reach about 5×10^{-9} torr. The first XPS spectra were then obtained. Then with the ion pump off the pressure was raised to 5×10^{-5} torr with argon and the ion gun operated for an interval. The chamber was then pumped back to about 5×10^{-9} torr and the XPS spectra again recorded. This procedure was continuously repeated with sputtering times varying from 5 minutes to 30 minutes. Thus the bulk of the film could be analyzed or the interface composition determined as a function of depth. The latter is a depth profile.

RESULTS AND DISCUSSION

Chromium Boride

Target history. - A CrB_2 target was exposed to air for 2 days. Then a series of films was prepared. Successive films were deposited after increasing target sputter cleaning times. The vacuum system was not opened between depositions. No bias voltage was used.

Figure 2 shows the boron XPS spectra of these films. The film deposited after only 30 minutes of target sputtering contains virtually no boride but only boron oxide. The amount of boride increases with increasing target sputtering. The chromium spectrum showed a similar change for a chromium oxide to a boride as the series progressed. It was observed that the color of the glow discharge in the sputtering system changed as the series progressed. It was first a purple color and changed gradually to a brighter blue. Furthermore it was noticed that the base pressure in the vacuum system when the argon flow was stopped was an appreciable part of the sputtering pressure early in the series becoming negligible at the end.

The friction coefficients shown in Fig. 2 are from pin and disk tests with a 304 stainless steel rider at 25 gram load (3). Apparently the film composition has a strong effect on its friction. The presence of oxides is detrimental.

The CrB_2 target is a particularly porous pressed compact. It is concluded that the results here are due to degassing of this porous target. This effect has been observed with hot pressed targets by Vossen (12). In all the work reported hereinafter, the importance of degassing the target was recognized. It was found that by monitoring the color of the glow discharge and only depositing coatings after the color had stabilized, reproducible coatings be applied. No other target showed as great a propensity to outgas as did the CrB_2.

Substrate bias. - Coatings were prepared with the substrate held at bias voltages from 0 to -500 volts. In general the XPS spectra from these coatings showed a pair of clearly resolved boron (1s) peaks at 187.6 and 191.5 eV similar to those of Fig. 2 and a broad chromium (2p 3/2 peak). The Cr(2p 3/2) peak was resolved using the analog curve resolver into a CrB_2 peak at 573.6 eV and a broad Cr_2O_3 peak at 576.0 eV. The broadening of the chromium peak in Cr_2O_3 is commonly observed (13). In addition to the chromium and boron spectra, the O(1s) and C(1s) spectral lines were recorded.

In order to show the effect of bias voltage on chromium boride stoichiometry the ratio of the 187.6 eV B(1s) and 573.6 eV Cr(2p 3/2) peak heights was plotted as a function of bias voltage and compared to the same ratio for the CrB_2 standard. The result is Fig. 3(a). Figure 3(b) shows the variation in oxygen peak height with bias voltage. The boron oxide B(1s) peak (191.5 eV) decreases exactly as the oxygen peak does. The carbon peak was unaffected by biasing.

It can be seen from Fig. 3 that bias voltages up to -300 volts improved the stoichiometry of the chromium boride although the composition of the target material is never achieved.

Deposition time. - Figure 3 also shows the effect of reducing the deposition time (and hence the film thickness) from 20 minutes to 10 minutes. There is a distinct reduction in oxygen content and a corresponding improvement in stoichiometry at lower bias voltages. At -300 and -500 volts there is no difference.

Figure 4 shows a clear correlation between compound stoichiometry and the oxygen content of the film. However, it is also clear from Figs. 3 and 4 that something other than oxygen influences stoichiometry at -500 volts bias. The chromium boride never reaches the target stoichiometry and at high bias voltage it deteriorates in spite of decreasing oxygen content.

Sputtering power. - A CrB_2 film was deposited with -500 volts bias for 10 minutes at 600 watts target power instead of the 300 watts used for the other films. Figure 5 shows how the oxygen, boron, and boride peak heights varied with depth in this film. Figure 6 shows the change in the Cr(2p 3/2) peak with depth. The peak has been resolved into its oxide and boride components. The coating is entirely chromium oxide and boron oxide in its outer surface. After 80 minutes of ion beam etching the oxide decreases and some boride appears. After 120 minutes of etching, the film is primarily boride. At this depth the boride to chromium peak height ratio is identical to that of -500 volts bias films deposited at 300 watts.

Summary of CrB_2 results. - While an initial presputtering of targets is common practice in order to clean the surface and reach equilibrium, the degree of outgassing from a porous compact like CrB_2 necessitates extreme care. Deposited films have been found to be oxidized to some degree due to outgassing caused by insufficient presputtering of the target, long sputtering times, and high power levels.

Bias sputtering had two effects on the CrB_2 coatings. Oxides were decreased and the stoichiometry of the chromium boride improved by increasing the bias voltage from 0 to -300 volts. Stoichiometry was adversely affected by bias voltages from -300 to -500 volts

Molybdenum Disulfide

The MoS_2 target was easily degassed by presputtering. The color of the glow discharge stabilized quickly and the base

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pressure was low even when the target was hot. The film compositions were very reproducible.

Figure 7(a) shows the effect of substrate bias on film stoichiometry as indicated by the sulfide (162.8 eV) to molybdenum peak height ratio. The 162.8 eV peak was the only detectable sulfur peak. Figure 7(b) shows the oxygen peak height as a function of bias voltage.

At zero bias voltage the deposited film is MoS_2. There is some oxygen present probably as an oxide of molybdenum. This would account for the slightly low value of the sulfide to molybdenum ratio. No sulfates were detected. The sulfur concentration decreases with increasing bias voltage until at -500 volts, there is very little sulfur present in the coating. The oxygen concentration also decreases initially, however, by -300 volts the oxygen level has begun to increase again and at -500 volts it is actually greater than it was at 0 volt.

The friction coefficient (3) in Fig. 7(c) shows the effect of the loss of sulfur. Comparison of Figs. 7(a) and (c) indicates that the film has low friction when the MoS_2 concentration is above about 75 percent and that the friction is high for MoS_2 concentrations below about 30 percent. There appears to be a minimum concentration near 50 percent that permits effective MoS_2 lubrication.

Discussion of Bulk Film Properties

It is proposed that oxygen contamination has two sources in the target. First, there is an oxidized layer at the surface. This source may be more important for pressed compacts than for cast targets because of the high surface to volume ratio of the compacts. The long cleanup times and the pure oxide that is deposited initially from the CrB_2 target is evidence for such an oxide layer as the initial source of oxygen contamination.

Once the initial oxide layer has been removed, the second source of oxygen is diffusion from the bulk of the target. Once again this is obviously especially significant for targets made of pressed powders. During the target cleanup, a region near the surface of the target is degassed. Films deposited after this are relatively free of oxide; however, there is always some residual contamination due to further diffusion from the bulk.

If the sputtering power is high, the target temperature will rise causing much more rapid diffusion. The result is a deterioration of the film as sputtering goes on. This was seen in the depth profile of the CrB_2 film deposited at 600 watts.

Even at lower power the oxygen continually diffuses to the surface, after the initial cleanup. Furthermore as sputtering progresses, the surface of the target gradually recedes into the more heavily contaminated bulk. Both of these things cause films with long deposition times to be more heavily oxidized films with shorter deposition times. This is clearly the case for the 20-minute CrB_2 films as opposed to the 10-minute films.

To summarize, pressed compact targets yield highly oxidized films because of their oxidized surface and included oxygen. Proper target preparation can remove the surface oxide and degas the surface region of the target allowing deposition of purer films. High power levels and long deposition times, by increasing diffusion rates and exposing more poorly degassed bulk material, cause more contaminated films. In any case, oxygen is always a significant contaminant in films deposited without substrate bias. This is evident in the curves of oxygen versus bias voltage for both materials tested.

When the substrate is biased with a negative voltage during deposition, there will be some sputtering of the substrate surface as the film is deposited. This will cause resputtering of atoms from the film. In a multicomponent film, such as those discussed here, the sputtering rates of the two components may differ. In that case the film will become deficient in the component with the higher sputtering yield.

Unfortunately, measured sputtering yields from multicomponent films are not available. However, by using the ion gun in the XPS system to sputter etch MoS_2 films it was determined that sulfur was sputtered more rapidly from these films than was molybdenum. The sulfur to molybdenum XPS peak height ratio decreased from 0.24 after 30 seconds of sputtering to 0.15 after 20 minutes sputtering. The CrB_2 film showed no comparable change in composition with sputtering time.

From these observations it is expected that the composition of MoS_2 would be strongly affected by bias voltage. That is, in fact, the case as can be seen in Fig. 7(a). The MoS_2 film shows an almost total loss of sulfur at -500 volts bias. There is some evidence of a small effect on CrB_2 in the decrease in peak height ratios at high bias voltage.

A second effect of bias voltage is the decrease in oxygen content of the films as the bias voltage is increased. This is a commonly observed phenomenon (14) and is of particular value for these pressed compact targets which tend to produce oxidized films. The reason for the preferential sputtering of oxygen is not known. It is known that many metal oxides are reduced by sputtering (15, 16) so that the sputtering yield for oxygen is apparently relatively high. In any case, removal of oxygen from the film as it is forming can improve the stoichiometry of the deposited compound as is the case for CrB_2.

The MoS_2 film is unique in showing an increase in oxygen content at high bias voltages. This may be because of the large decrease in sulfur content of the film. The free molybdenum remaining, which has a great oxygen affinity, could react with oxygen in the sputtering chamber or after exposure to air.

Thus the effect of biasing on film composition depends strongly on the particular compound being deposited and on the

choice of bias voltage. The stoichiometry of CrB_2 was improved by bias voltages up to -300 volts and degraded at -500 volts while the oxygen content decreased at all bias voltages. The use of bias voltages for MoS_2 drastically degraded the film stoichiometry and even caused an increase in oxygen content at -500 volts. In both cases good friction properties correlated with good stoichiometry.

Film Substrate Interface

When the bulk film properties were well controlled, it was found that films often failed by spalling during wear tests (17). Each film type was deposited on a preoxidized 440C substrate and on a sputter etched substrate with -300 volts bias. Depth profiles were made. Here the film constituents were determined in mole percent by methods described elsewhere (19). Oxidation of the substrate before deposition improved coating adhesion for some materials but not others. Figure 8 summarizes the results of tests on MoB_5 and Mo_2C reported in another paper at this conference (18). Coatings of both materials on sputter cleaned 440C give friction characteristic of the uncoated metal. The profilometer trace for the Mo_2C wear track in this case is characteristic of film failure by spalling (17). Indeed, in many cases the Mo_2C film peeled from the disk spontaneously. Oxidizing the 440C substrate prior to deposition improved the adhesion of Mo_2C dramatically as indicated by negligible wear. Preoxidation of the substrate had no effect on the Mo_2B_5 adhesion, however. These results suggested that depth profiles of the composition of the steel-film interface region in these coatings would be revealing.

Interfacial Oxides

Figure 9 shows a depth profile of Mo_2C on a sputter etched substrate. It has been observed previously that the main contaminants in sputtered refractory compounds are oxides. These oxides are a result of target degassing and are reduced by substrate bias. It can be seen here that even with substrate bias and without preoxidation of the surface there was an increase in the concentration of all oxides including Fe_3O_4 in the interface. This may have resulted from an initial burst of oxygen that had diffused to the target surface while the substrate was being sputter etched, or it could have been due to leaks at the feedthroughs for the manipulators that move the substrate under the target just before film deposition. The Fe_3O_4 concentration reached 15 to 25 percent in this case. The interfacial region is about 100 Å thick.

When the 440C is deliberately oxidized before film deposition, a thick heavy Fe_3O_4 layer is found in the interfacial region, but very little chromium oxide is found. In Fig. 10 a comparison is made between the iron 2p 3/2 and chromium 2p 3/2 at several depths in a Mo_2C film deposited on an oxidized 440C substrate. The outer layer of the oxide (etching depth of 375 Å) is iron rich. The area under the iron peak is more than 10 times the area under the chromium peak. In clean 440C the iron peak area is 4.7 times the chromium peak area. Midway through the oxide region (etching depth of 525 Å), the iron present is almost entirely oxidized while the chromium peak shows a substantial proportion of elemental (unoxidized). Since the ion etching process will tend to mix the film and reduce variation with depth, the outer oxide region is probably even more predominantly iron oxide than this analysis indicates.

Figure 11 is a depth profile of the Mo_2C film on oxidized 440C. The preoxidized region is 350 Å wide and there is penetration into the 440C substrate. This results in a less abrupt transition from 0 to 100 percent Fe than occurs on the unoxidized substrate.

Figure 12 is the depth profile of a Mo_2B_5 film on an oxidized 440C substrate. Comparison of Figs. 11 and 12 shows a difference in the nature of the interfacial oxide region. In Mo_2C, the molybdenum oxide and iron oxide are substantially mixed, while in the Mo_2B_5 interface there is pronounced layering of the constituents. Taken together with the adhesion data of Fig. 8 this suggests that good adhesion of these refractory coatings depends on the formation of a mixed oxide or spinel in the interfacial region. This would be in accord with early work on cermets (20) and much of the experience in the electronics industry (e.g., 21).

CONCLUSIONS

The XPS analysis of rf sputtered refractory coatings suggests the following:

1. The primary contaminant in these coatings is oxygen from the porous targets. The contamination can be severe enough that pure oxide coatings are deposited.

2. The presence of oxygen affects the stoichiometry of the refractory compound, itself.

3. Biasing the substrate during film deposition reduces the oxygen contamination and can improve stoichiometry. However back sputtering of the film can also degrade the stoichiometry. The exact effect is dependent on the compound being sputtered and the bias voltage selected.

4. Oxides of the film components and iron are always present at the coating-steel interface. However preoxidation of the steel produces a thicker and more dense iron oxide (~300 Å thick). In Mo_2C the oxides are mixed in the interfacial region while in Mo_2B_5 there is pronounced layering of the film and iron oxides. Since the adhesion of Mo_2C, is improved by preoxidation of the substrate while the adhesion of Mo_2B_5 is not, it is suggested that mixed oxide or spinel formation in the interface is important to refractory compound adhesion.

Finally, it should be pointed out that the particular coatings whose analysis is described here are representative of a large number of materials that have been investigated in detail (4, 7, 17, 18, 19). Those results also support the general conclusions drawn here.

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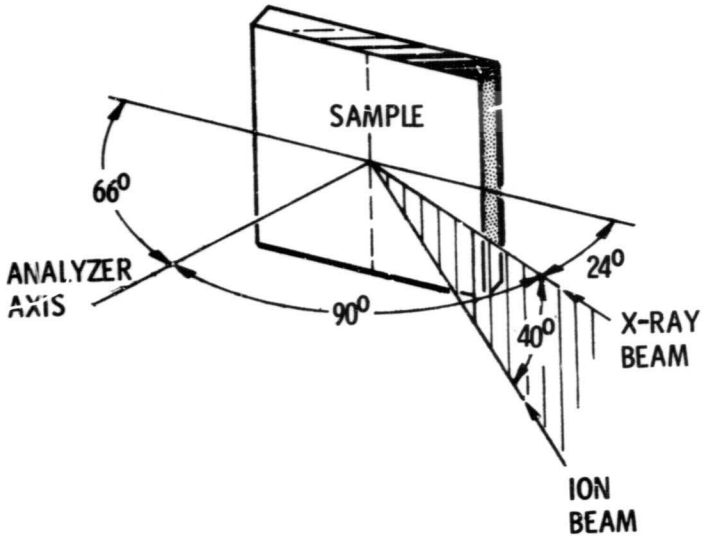
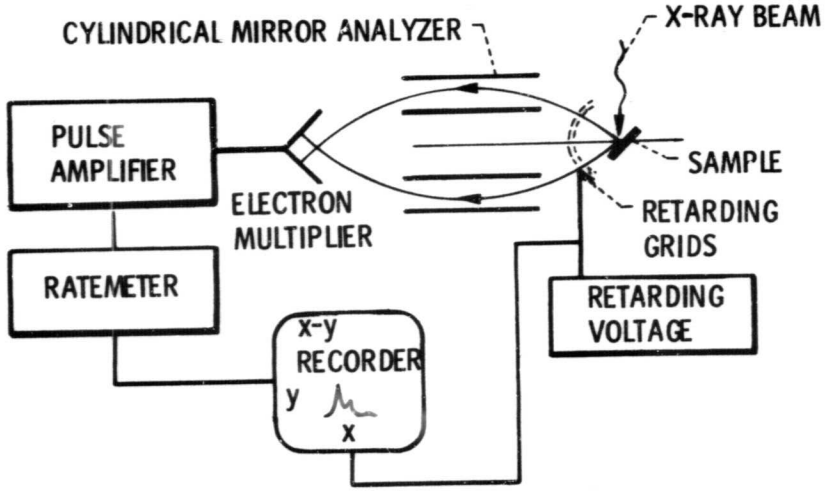


(a) GEOMETRY OF SYSTEM.



(b) BLOCK DIAGRAM.

Figure 1. - Configuration of XPS system.

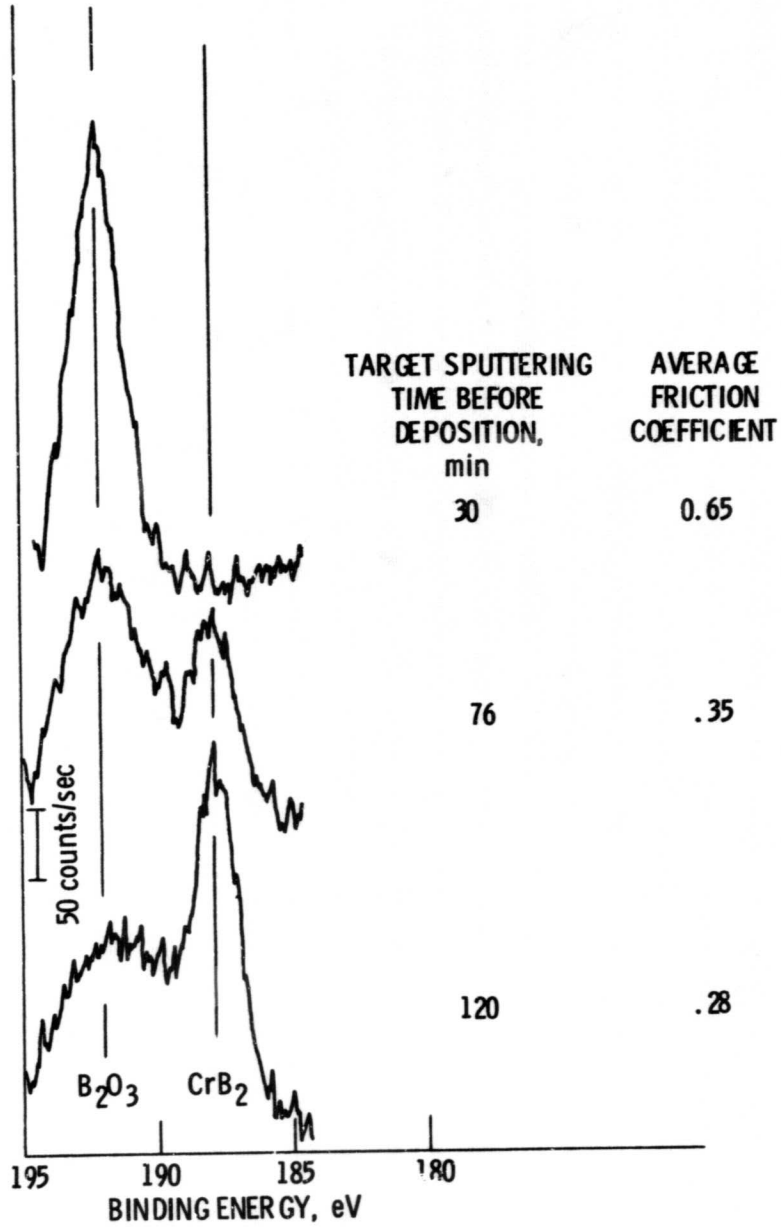


Figure 2. - Change in boron XPS peak and film friction with target use. CrB_2 target substrate grounded. Peaks recorded after 5-minute ion etching. Friction coefficients from reference 3.

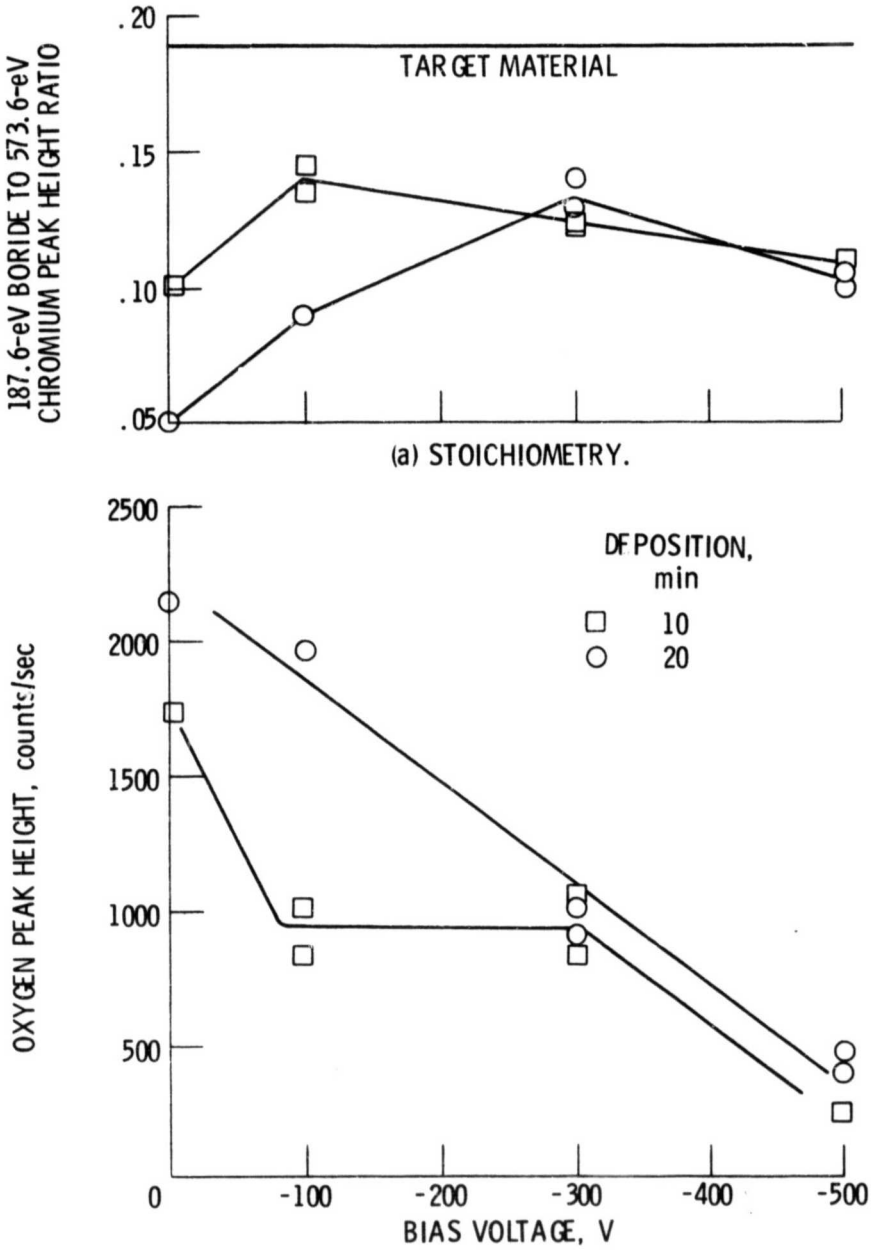


Figure 3. - Influence of bias voltage on CrB_2 coatings.

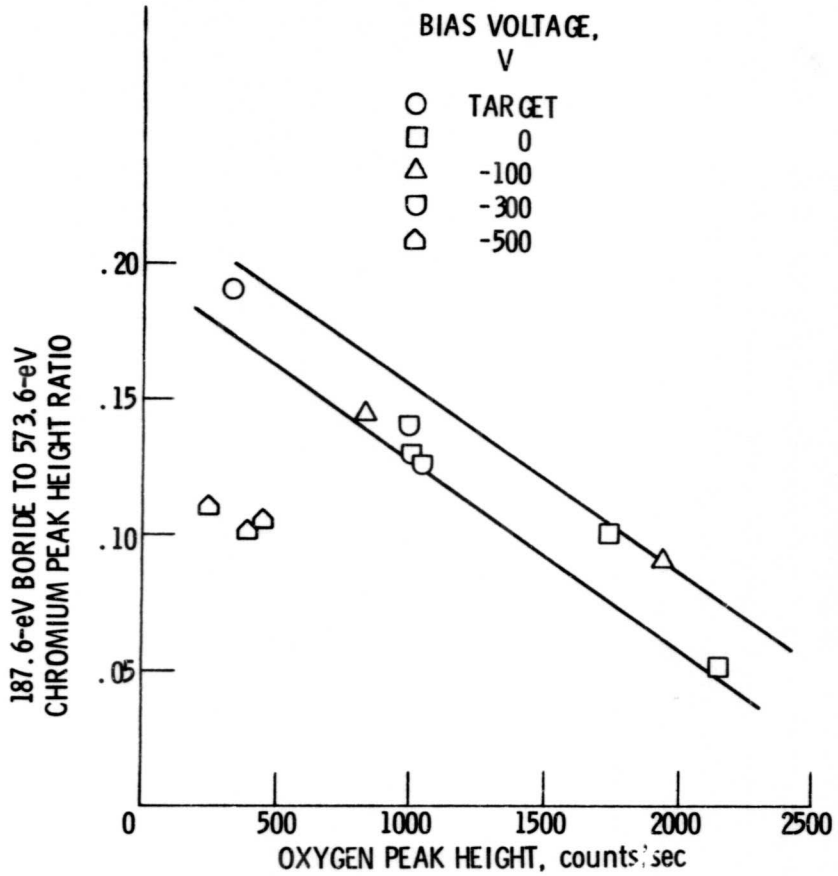


Figure 4. - Boride- to chromium ratio for sputtered CrB_2 films as a function of oxygen content.

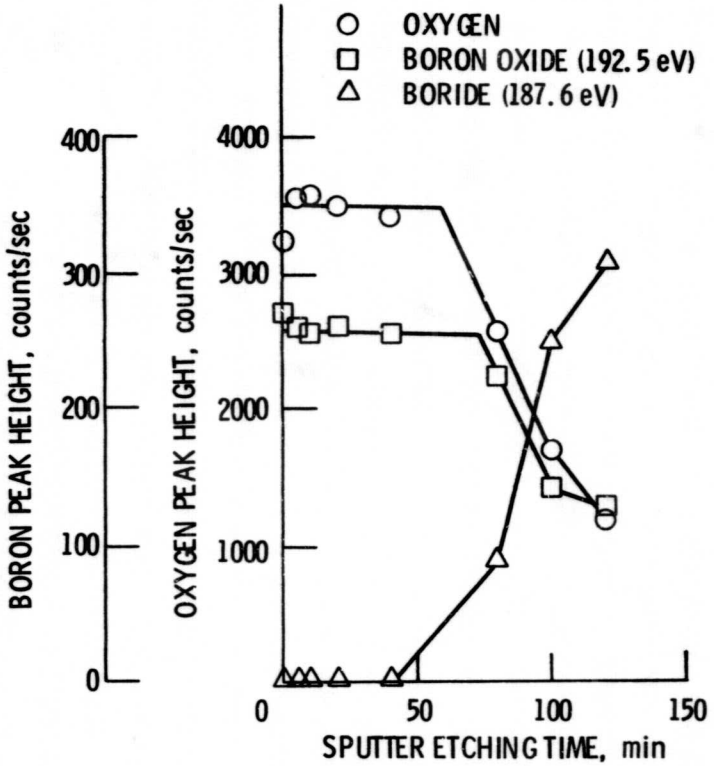


Figure 5. - XPS peak heights as a function of 2-keV argon ion etch time for CrB_2 coating; 600 watts; 10 minutes deposition time; -500 volts bias.

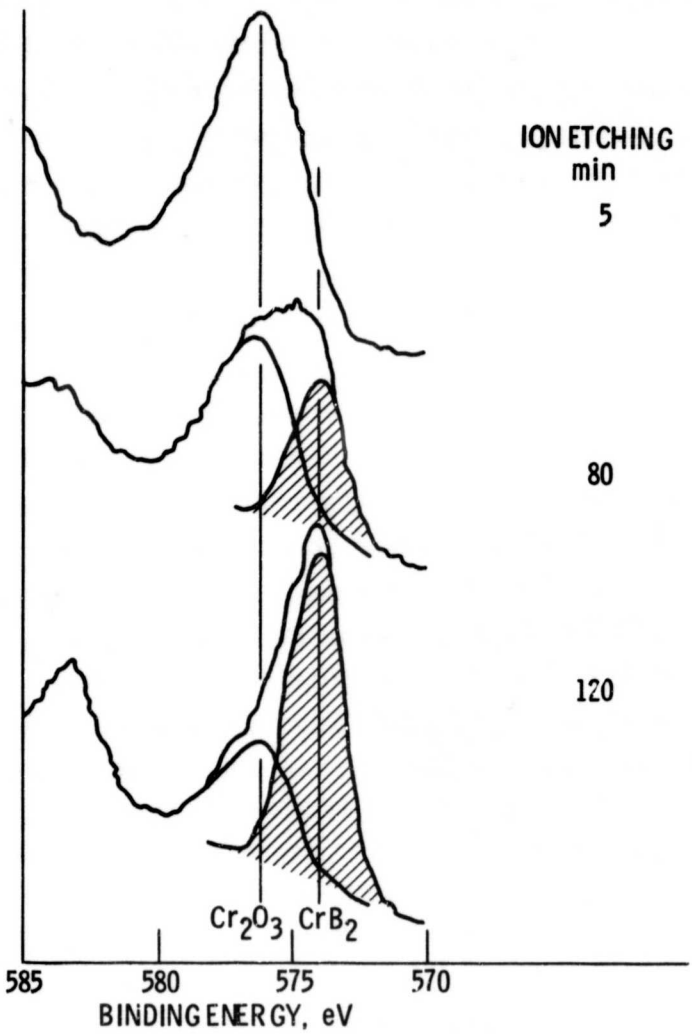
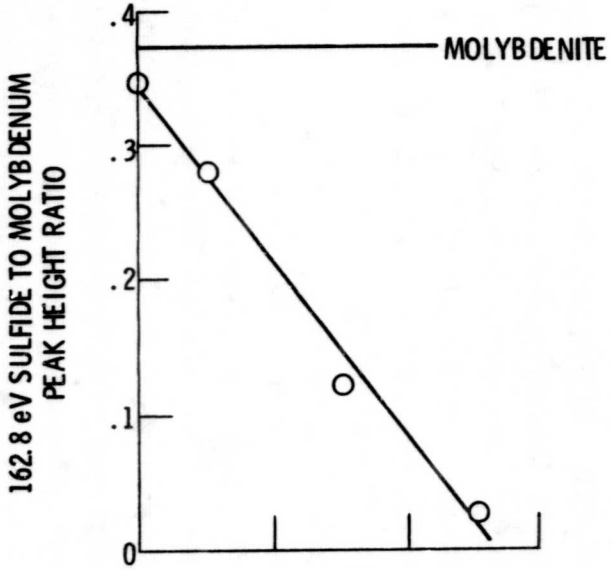
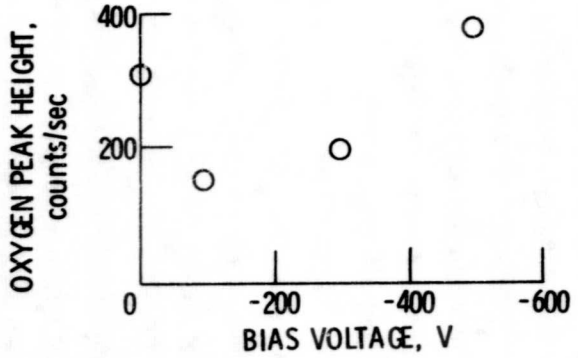


Figure 6. - Cr(2p 3/2) XPS peak in CrB_2 film sputtered at 600 watts, -500 volts bias for 10 minutes sputter etched for 5, 80, and 120 minutes. (See table I for Cr_2O_3 and CrB_2 reference values. Curve resolver used to determine component peaks shown.)

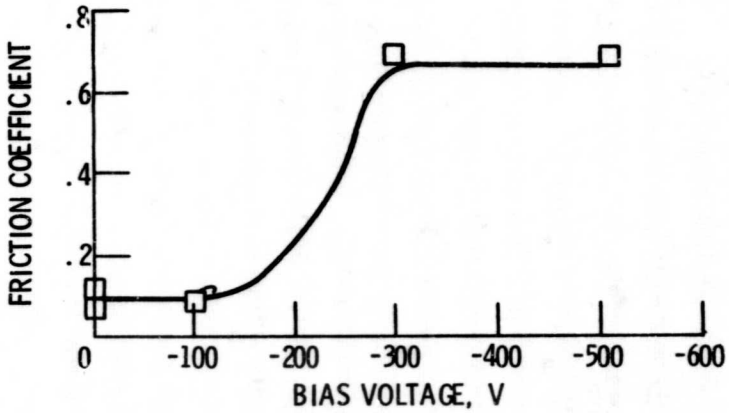


(a) STOICHIOMETRY.



(b) IMPURITIES.

Figure 7. - Influence of bias voltage on MoS_2 coatings. Friction data from reference 3.



(c) FRICTION COEFFICIENT.

Figure 7. - Concluded.

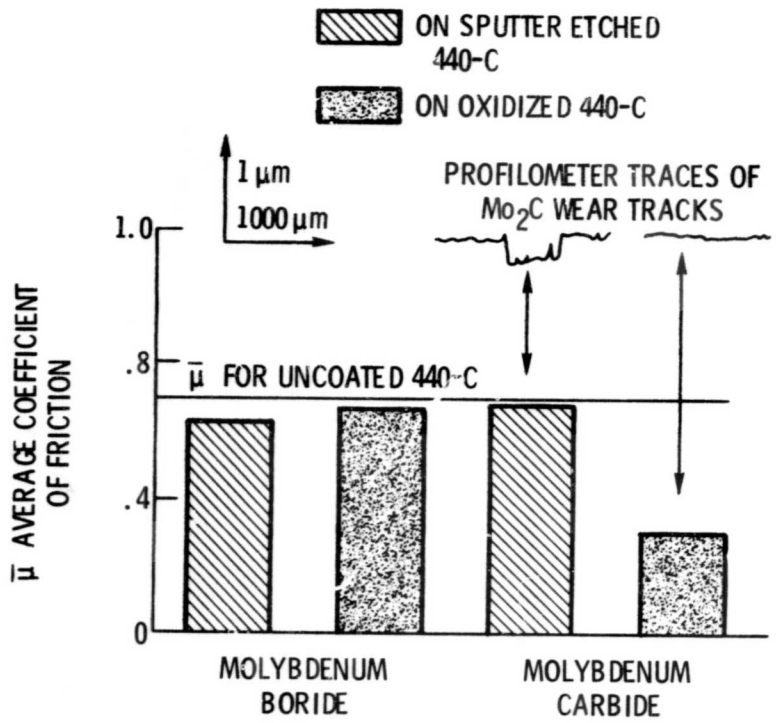


Figure 8. - Friction and wear behavior of molybdenum boride and molybdenum carbide RF sputtered coatings on sputter etched or oxidized 440-C substrates. -300 V bias. Data from reference 18.

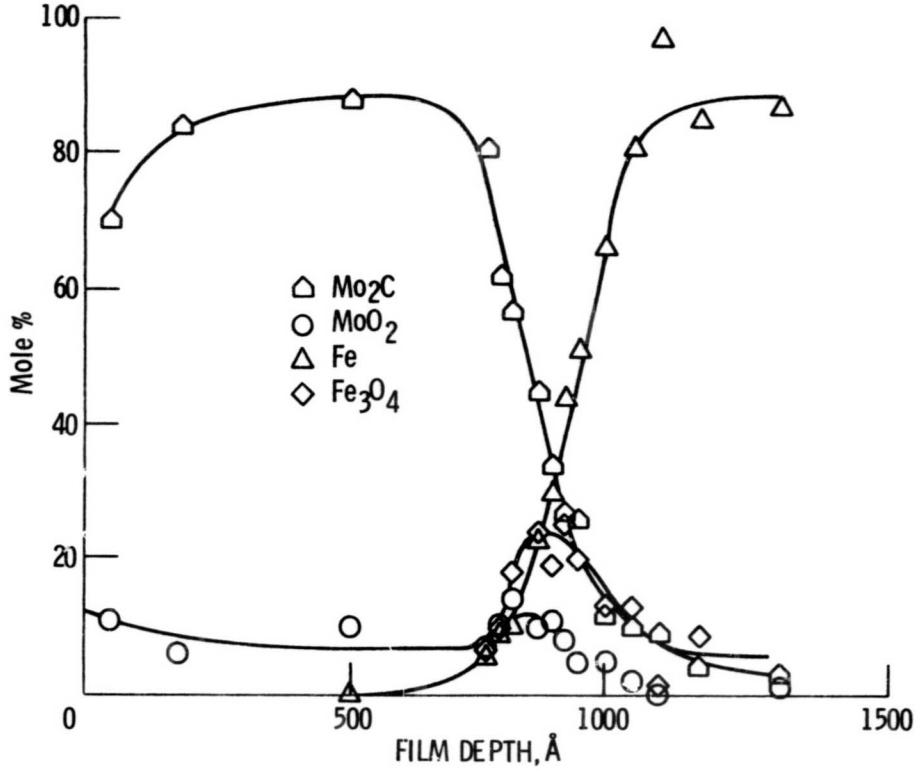


Figure 9. - Depth profile of Mo_2C radiofrequency sputtered onto sputter-etched 440C substrate. Bias, -300 volts.

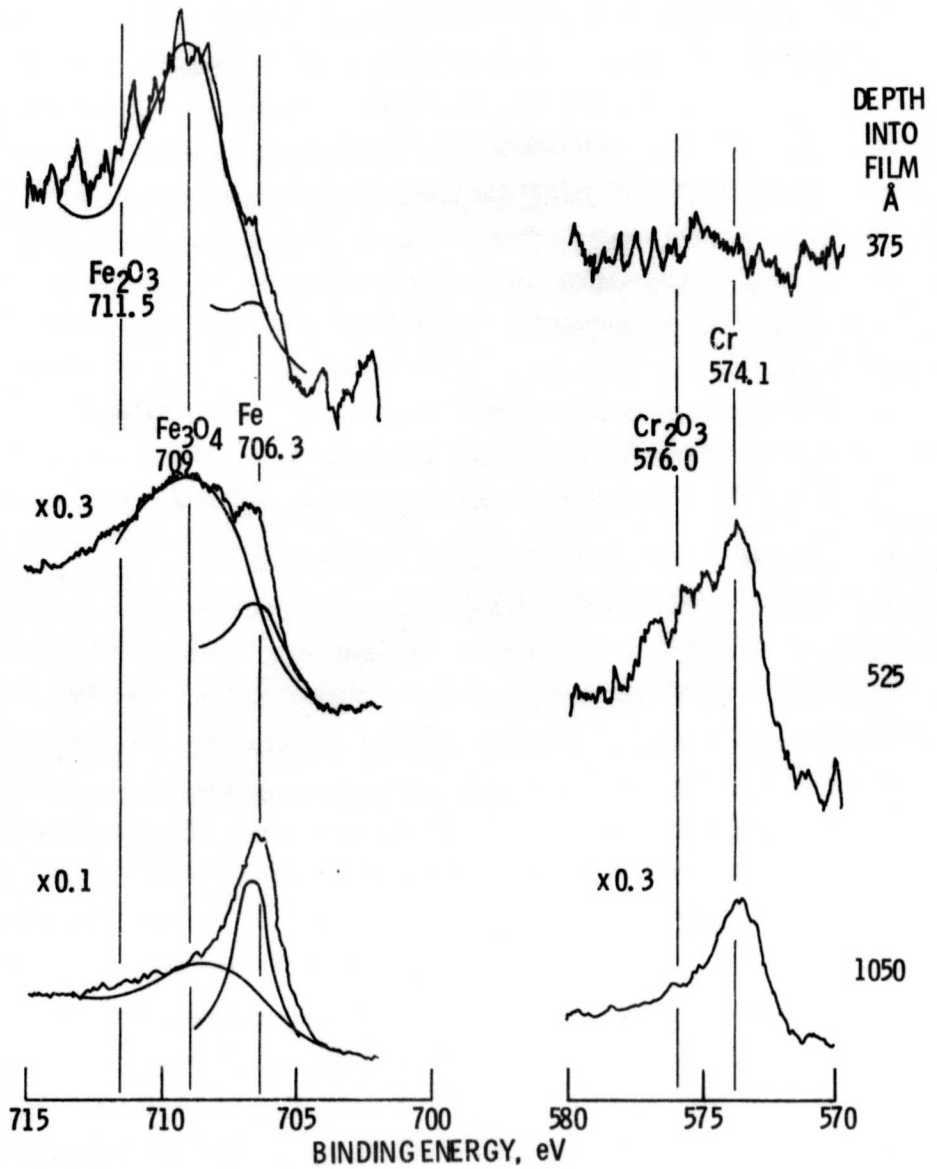


Figure 10. - Iron (Fe $2p_{3/2}$) and chromium (Cr $2p_{3/2}$) XPS peaks at different depths in Mo_2C film radiofrequency sputtered onto an oxidized 440C steel substrate. Bias, -300 volts; vertical scale, arbitrary units.

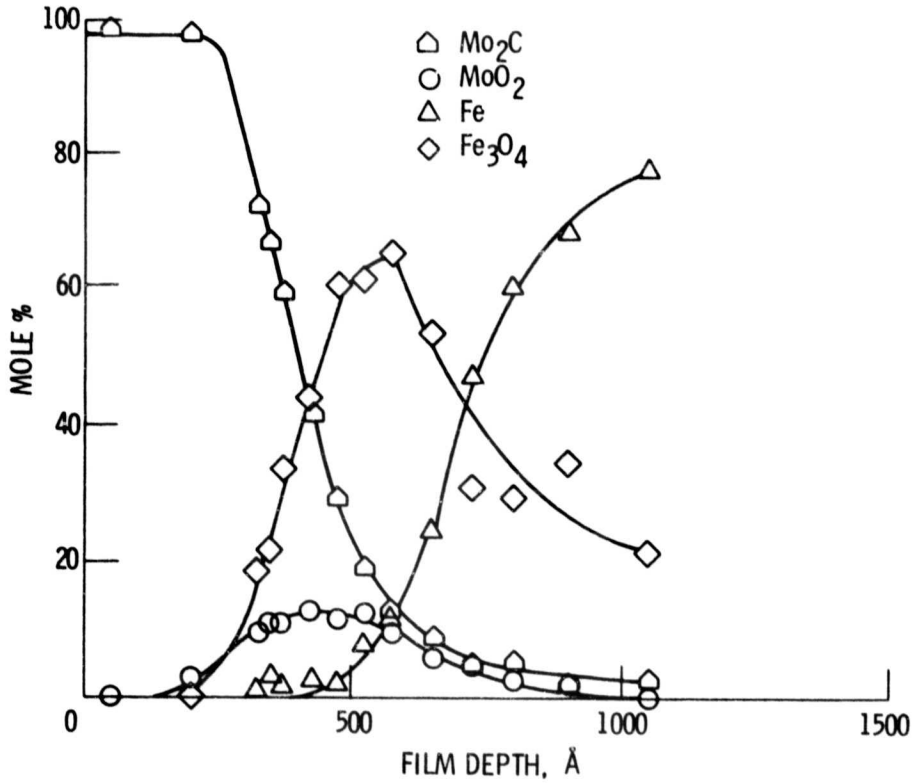


Figure 11.- Depth profile of Mo_2C radiofrequency sputtered onto oxidized 440C substrate. Bias, -300 volts.

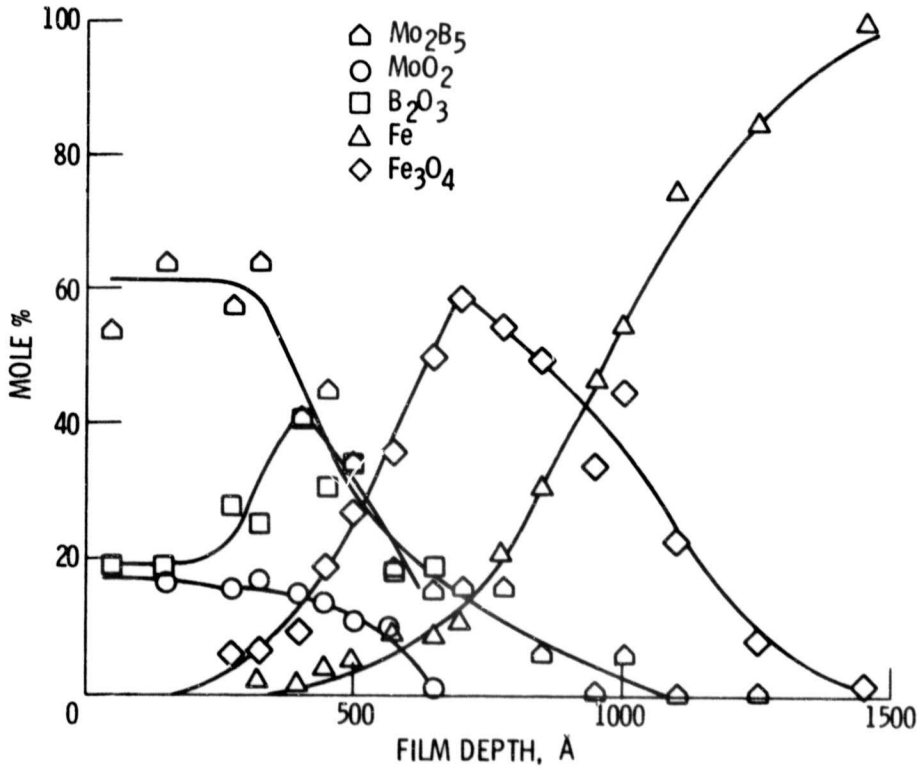


Figure 12.- Depth profile of Mo_2B_5 radiofrequency sputtered onto oxidized 440C substrate. Bias, -300 volts.